On the origin and contribution of the diamagnetic term in 4-component relativistic calculations of magnetic properties.

Aucar, G.A.; Saue, T.; Visscher, L.; Jensen, H. J. Aa.

published in
Journal of Chemical Physics
1999

DOI (link to publisher)
10.1063/1.479181

document version
Publisher's PDF, also known as Version of record

On the origin and contribution of the diamagnetic term in four-component relativistic calculations of magnetic properties

G. A. Aucar,[a] T. Saue, L. Visscher,[b] and H. J. Aa. Jensen[c]
Department of Chemistry, Odense University, Campusvej 55, Odense M, Denmark

(Received 21 July 1998; accepted 29 December 1998)

The relativistic Dirac Hamiltonian that describes the motion of electrons in a magnetic field contains only paramagnetic terms (i.e., terms linear in the vector potential **A**) while the corresponding nonrelativistic Schrödinger Hamiltonian also contains diamagnetic terms (i.e., those from an A^2 operator). We demonstrate that all diamagnetic terms relativistically arise from second-order perturbation theory and that they correspond to a ''redressing'' of the electrons by the magnetic field. If the nonrelativistic limit is taken with a fixed no-pair Hamiltonian (no redressing), the diamagnetic term is missing. The Schrödinger equation is normally obtained by taking the nonrelativistic limit of the Dirac one-electron equation, we show why nonrelativistic use of the A^2 operator is also correct in the many-electron case. In nonrelativistic approaches, diamagnetic terms are usually considered in first-order perturbation theory because they can be evaluated as an expectation value over the ground state wave function. The possibility of also using an expectation value expression, instead of a second-order expression, in the relativistic case is investigated. We also introduce and discuss the concept of ''magnetically balanced'' basis sets in relativistic calculations. © *1999 American Institute of Physics.* [S0021-9606(99)30213-0]

I. INTRODUCTION

If we want to study molecules in an external magnetic field or if we take nuclear spins into account we need to consider the interaction of electrons with a magnetic field. The theoretical description of such systems is complicated by the fact that magnetic fields break the time reversal symmetry of the system. Under the usual experimental conditions the magnetic fields are weak compared to the electric field due to the nuclei and we may, therefore, expect that their effects are well described by perturbation theory. For closed-shell systems the first-order energy correction is zero due to time reversal symmetry, so that the lowest order contribution is the second-order energy correction $E^{(2)}$. In the usual nonrelativistic Rayleigh–Schrödinger perturbation theory with exact solutions to the zeroth-order Hamiltonian, the second-order energy correction has the general sum-over-states form

$$E^{(2)}=\sum_{n\neq 0}\frac{\langle 0|H_1|n\rangle\langle n|H_1|0\rangle}{E_0-E_n}+\langle 0|H_2|0\rangle, \tag{1}$$

where H_1 is linear in the perturbation and H_2 is quadratic in the perturbation. Formally magnetic fields **B** are introduced by applying the minimal electromagnetic coupling, i.e., [in SI units]

$$\mathbf{p}\rightarrow\pi=\mathbf{p}+e\mathbf{A}, \tag{2}$$

where **A** is a vector potential corresponding to **B**. Within the framework of nonrelativistic theory one obtains perturbation operators that are linear and quadratic in the vector potential

$$H_1^{\mathrm{NR}}=\frac{e}{2m}(\mathbf{p}\cdot\mathbf{A}+\mathbf{A}\cdot\mathbf{p}) + \frac{eg_e}{2m}i\mathbf{s}\cdot(\mathbf{p}\times\mathbf{A}+\mathbf{A}\times\mathbf{p}) \quad \text{and} \quad H_2^{\mathrm{NR}}=\frac{e^2}{2m}\mathbf{A}^2, \tag{3}$$

where **s** is the electronic spin operator and g_e is the electronic *g*-factor, corrected for QED effects. [Apart from the deviation of the electronic *g*-factor from 2, which is a QED (quantum electrodynamics) effect, these operators follow from the nonrelativistic limit of the Dirac equation given in Eq. (9) below, using that $\mathbf{s}=\sigma/2$.] The perturbation operator linear in the vector potential contributes to the first term of $E^{(2)}$ which has the form of a sum-over-states and represents the paramagnetic contribution (which, for example, for nuclear spin–spin couplings give the spin-independent paramagnetic spin–orbit as well as the spin-dependent spin–dipole/Fermi contact contributions). The perturbation operator quadratic in the vector potential generates the second term of $E^{(2)}$ which has the form of an expectation value and is denoted the diamagnetic term.

Within the framework of four-component relativistic theory only a single perturbation operator, linear in the vector potential, appears

$$H_1^{\mathrm{R}}=ec(\alpha\cdot\mathbf{A}). \tag{4}$$

As we shall see later, Eq. (1) must be generalized for the many-electron case and then takes the form of a linear response equation, but this generalization does not affect the arguments here. Apparently then, there is no diamagneticlike

[a]Permanent address: Physics Department, Exact and Natural Science Faculty-UNNE, Av. Libertad 5300, 3400 Corrientes, Argentina.
[b]Permanent address: Department of Chemistry, Vrije Universiteit Amsterdam, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands.
[c]Electronic mail: hjj@dou.dk

contribution in the relativistic domain. Sternheim[1] has, however, shown that in this framework and for one-electron systems the diamagnetic contribution is approximately equal to the part of the first term in $E^{(2)}$ which involves summation over positronic orbitals. Pyykkö[2] has extended this analysis to many-electron systems by generalizing the summation over positronic orbitals to the summation over positronic states. We will, in this article, demonstrate that these assumptions should be taken with care within four-component theory. The problem is as follows: In the standard treatment of the many-electron problem the wave function of a given electronic state is expressed as a sum of Slater determinants of one-particle electronic orbitals. In the relativistic case the one-particle basis contains solutions of both positive and negative energy. We will follow the no-pair approach of QED[3] by identifying the negative energy solutions as positronic orbitals that are unoccupied in the electronic ground states of molecules. The many-electron wave function is then expanded in terms of Slater determinants consisting of electronic orbitals only. In order to treat the external magnetic field in the framework of sum-over-states perturbation theory it would be necessary to include the complete set of solutions of the zeroth-order Hamiltonian, also those containing mixed states (Slater determinants built from both electronic and positronic orbitals). This is inconsistent because it is in contradiction with the no-pair approach of QED. In addition, according to the QED interpretation of the negative energy solutions inclusion of these mixed states is unphysical because they represent states with different *charge* from the zeroth-order wave function. Mathematically they are, however, needed for a complete description of the perturbed wave function.

We will show that this apparent contradiction can be overcome by using response theory instead of the sum-over-states formalism. Within this framework one may include the positronic degrees of freedom without explicitly treating the determinants that contain positronic orbitals. In this way one prevents problems with the unboundedness of the Dirac operator, like the Brown–Ravenhall disease.[4] We shall also carefully investigate whether it makes any sense to think in terms of diamagneticlike contributions in four-component relativistic molecular calculations, and we shall define a sequence of approximations leading to the reformulation of the diamagnetic contribution in terms of an expectation value. Such a reformulation begins with a separation of the linear response function (at the Dirac–Hartree–Fock level) into two terms corresponding to e-e orbital rotations (between occupied and virtual electronic orbitals) and e-p rotations (between occupied electronic and virtual positronic orbitals). The diamagnetic term arises from the latter term. We will further investigate the validity of the expectation value exposition by numerical results. We have chosen to focus on the indirect spin–spin couplings which arise in nuclear magnetic resonance (NMR) spectroscopy.

II. THEORY

A. Background

Our point of departure is Dirac's relativistic wave equation.[5] An inherent complication of this equation is that it describes two kinds of particles, namely electrons and positrons. In the absence of external fields the spectrum of the Dirac operator splits into two branches, corresponding to free electrons and free positrons. With the introduction of an external field the spectrum is modified with the possible appearance of bound electronic or positronic states.

In this paper we consider molecular systems and interaction energies much lower than the $2mc^2$ required for the creation of real electron–positron pairs. The relativistic treatment of such systems is usually done within a no-pair approximation, in which the Dirac operator is embedded between projection operators onto the electronic states. Sucher[6] has discussed various choices of no-pair Hamiltonians for molecular applications. One choice is to define the projection operators in terms of the free electronic solutions, whereas another possibility is to use solutions of the attractive electric field of stationary nuclei. The latter choice is referred to as the Furry[7] picture. Neither of these no-pair Hamiltonians is optimal for the solution of many-electron molecular systems, since the projection operators do not take into account the repulsive interaction of the electrons. The Furry projection operators are, however, expected to perform better than the free particle projections since they represent a better approximation to the actual potential of the system. Mittleman[8] has pointed out that a better choice of projections in many-electron Dirac–Hartree–Fock calculations is obtained by inclusion of the mean-field electron repulsion potential. The projection operators are then continuously updated during the iterative solution of the Dirac–Hartree–Fock equations and find their final form at convergence.

The no-pair projection operators are thus defined by a specific choice of the external potential. Within the no-pair approximation focus is on the electronic states. It is important, however, to realize that the external potential defines what are electronic solutions and what are positronic solutions. Any change in the external potential results in a redressing of electrons and positrons such that an electronic solution of a given potential will have both electronic and positronic contributions in terms of solutions of a different potential. This has profound implications for the application of no-pair Hamiltonians, as has been discussed by Heully *et al.*[9] Consider electronic solutions of an external potential V_1. As stated above, these solutions will have both electronic and positronic contributions in terms of solutions of a different external potential V_2 (and *vice versa*). We now consider the solutions for the system in the presence of the external potential V_1 using a no-pair Hamiltonian with projection operators defined by the external potential V_2. Clearly the no-pair ''electronic'' solutions obtained this way differ from the ''true'' electronic solutions of potential V_1 since some positronic contributions in terms of solutions of V_2 are missing and some electronic contributions in terms of V_2 have been introduced that correspond to positronic contributions in terms of V_1. From these considerations it is obvious that the optimal choice of projection operators for a no-pair Hamiltonian is the *actual* external potential of the system under study. This, however, requires knowledge of the solutions beforehand or an iterative procedure.

There are cases within the no-pair approximation in

which it is not possible or not convenient to have projection operators in terms of the actual potential of the system. In perturbation theory the solutions of the full Hamiltonian are expanded in terms of the solutions of a zeroth-order Hamiltonian H_0, and within the no-pair approximation the summation in the second-order energy expression $E^{(2)}$ is limited to electronic solutions only. The perturbative solutions will then approximate the solutions of the full Hamiltonian embedded in projection operators defined with respect to the potential of the zeroth order Hamiltonian and not the true solutions of the full Hamiltonian. We will demonstrate in this paper, both by theory and by calculations, that in the case of magnetic properties the missing part of the second-order energy correction corresponds to the diamagnetic term.

The positronic degrees of freedom are thus required for a proper perturbational treatment of magnetic properties in four-component theory. It is, however, important to realize that positronic contributions that are introduced in the perturbation expression above are *not* meant to take into account interaction of the zeroth-order electronic state with other states containing electrons and positrons, as in QED, but only to obtain *full relaxation* of the reference electronic state to the effect of the perturbation. There appears to be a lot of confusion in the literature on this point. As pointed out in the introduction, by resorting to response theory we an take into account the full modification of the one-particle basis by the external magnetic field without having to explicitly treat the problematic mixed states of electronic and positronic orbitals. In Sec. II C we shall investigate the many-electron case, but we shall first turn to one-electron systems to see the difference between a variational and a perturbational treatment of magnetic properties.

B. One-electron case

In this section we review how the diamagnetic term stems from the inclusion of the positronic eigenstates of the zeroth order Hamiltonian in the perturbative second-order energy expression within the sum-over-states scheme, and we analyze in detail the error we introduce by approximating this term with an expectation value in the relativistic case.

1. Exact solution and nonrelativistic limit

As background for the following discussion we first summarize a typical treatment of how the diamagnetic term may be obtained in the nonrelativistic limit by elimination of the small component. Consider the solutions of the Dirac equation for a molecular one-electron system in the presence of an external magnetic field represented by a vector potential **A**. The full electronic Dirac equation reads

$$\begin{bmatrix} V & c(\sigma\cdot\pi) \\ c(\sigma\cdot\pi) & V-2mc^2 \end{bmatrix}\begin{bmatrix} \psi^L(\mathbf{A}) \\ \psi^S(\mathbf{A}) \end{bmatrix}=E_{\mathbf{A}}\begin{bmatrix} \psi^L(\mathbf{A}) \\ \psi^S(\mathbf{A}) \end{bmatrix}, \tag{5}$$

in which the mechanical moment is $\pi=\mathbf{p}+e\mathbf{A}$. We have explicitly indicated that the eigenfunctions and eigenvalues of the Dirac equation depend on the external magnetic field. The large and small components of *exact* solutions of this equation are related by

$$\psi^S(\mathbf{A})=\frac{1}{2mc}k(E_{\mathbf{A}})(\sigma\cdot\pi)\psi^L(\mathbf{A}), \tag{6}$$

in which

$$k(E_{\mathbf{A}})=\left[1+\frac{E_{\mathbf{A}}-V}{2mc^2}\right]^{-1}. \tag{7}$$

In the nonrelativistic limit $c\to\infty$ and for electronic states $k(E_{\mathbf{A}})\to 1$. In the absence of an external vector potential **A** one then obtains the standard kinetic balance condition. Now, however, there is a magnetic component to the coupling of the large and small components.

Inserting relation (6) into Eq. (5) one obtains an equation in terms of the large components only with the magnetic terms included

$$\left\{(V-E_{\mathbf{A}})+(\sigma\cdot\pi)\frac{k(E_{\mathbf{A}})}{2m}(\sigma\cdot\pi)\right\}\psi^L(\mathbf{A})=0. \tag{8}$$

Considering the nonrelativistic limit the final expression is

$$\left\{(V-E_{\mathbf{A}})+\frac{1}{2m}p^2+\frac{e}{2m}[\sigma\cdot\mathbf{p},\sigma\cdot\mathbf{A}]_+ +\frac{e^2}{2m}A^2\right\}\psi^L(\mathbf{A})=0, \tag{9}$$

where the third and fourth terms are the nonrelativistic perturbation operators in Eq. (3). It is seen that the diamagnetic term $(e^2/2m)A^2$ appears naturally in this way.

2. Perturbational approach and nonrelativistic limit

Consider next the perturbative solution of this Dirac equation. We choose

$$H_1=ec(\alpha\cdot\mathbf{A}), \tag{10}$$

as the perturbation and the solutions of

$$\begin{bmatrix} V & c(\sigma\cdot\mathbf{p}) \\ c(\sigma\cdot\mathbf{p}) & V-2mc^2 \end{bmatrix}\begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix}=E_{\mathbf{A}=0}\begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix}, \tag{11}$$

as the zeroth-order solutions. Note that the small and large components of the zeroth-order Hamiltonian are now related by

$$\psi^S=\frac{1}{2mc}k(E_{\mathbf{A}=0})(\sigma\cdot\mathbf{p})\psi^L, \tag{12}$$

which is different from Eq. (6). This has important consequences for the perturbative solution of the full Hamiltonian.

In order to describe the difference between the exact solution in Eq. (5) and the zeroth order $(\mathbf{A}=0)$ solution in Eq. (11) by perturbation theory, it is obvious that the sum over n in the $E^{(2)}$ expression of Eq. (1) should include both the positive and negative energy solutions of Eq. (11), that is, both the electronic and the positronic solutions. The relativistic second-order correction to E in Eq. (1) can for one-electron systems thus be separated into two terms

$$E^{(2)}=E_e^{(2)}+E_p^{(2)}$$
$$=\sum_{n\neq 0}\frac{\langle 0|H_1|n\rangle\langle n|H_1|0\rangle}{E_0-E_n}+\sum_{\bar{n}}\frac{\langle 0|H_1|\bar{n}\rangle\langle\bar{n}|H_1|0\rangle}{E_0-E_{\bar{n}}}, \tag{13}$$

where we have written for clarification an explicit summation over electronic (n) and positronic ($\bar{n}$) *one-particle* states. By comparison with Sec. II B 1 we can now identify the $E_e^{(2)}$ term as the standard perturbation term corresponding to a fixed no-pair Hamiltonian, while the $E_p^{(2)}$ term describes the additional redressing of the electrons caused by the positronic degrees of freedom in response to the external magnetic field. (cf. the discussion in Sec. II A). Considering only the positive energy eigensolutions, it has been shown that one obtains only the paramagnetic contributions, whereas diamagnetic contributions are absent.[2,10,11] Hence, in the case of for example the indirect spin–spin coupling constant J one obtains the paramagnetic spin–orbit (PSO), Fermi contact (FC), and spin–dipolar (SD) terms. The diamagnetic spin–orbit (DSO) term is not contained in this part of the second-order correction to E.

Sternheim stated[1] that the diamagnetic contribution is obtained from the second term $E_p^{(2)}$ by the following approximations and assumptions (his ''states'' are one-particle states, i.e., spinors):

1. all $E_0-E_{\bar{n}}^-$ are replaced by $2mc^2$;
2. the explicit summation over positronic states is replaced by the resolution of the identity; and
3. all components of the vector potential $\mathbf{A}$ commute.

One then directly obtains an expression that resembles the diamagnetic contribution in the nonrelativistic domain

$$E_p^{(2)} \approx \frac{e^2}{2m}\langle 0|A^2|0\rangle. \tag{14}$$

In this formula A^2 is a diagonal four-component operator. Taking the nonrelativistic limit of this expression makes the small component of the wave function zero and yields the nonrelativistic diamagnetic expression in terms of the large component wave function that then becomes the nonrelativistic wave function. We shall now analyze the validity of this approach.

The summation over positronic states can be reexpressed in the following way:

$$\sum_{\bar{n}} \frac{\langle 0|H_1|\bar{n}\rangle\langle\bar{n}|H_1|0\rangle}{E_0-E_{\bar{n}}^-} = \frac{1}{2mc^2}\left[\sum_{\bar{n}} \langle 0|H_1|\bar{n}\rangle\langle\bar{n}|H_1|0\rangle - \sum_{\bar{n}} \langle 0|H_1|\bar{n}\rangle\langle\bar{n}|H_1|0\rangle\left(\frac{E_0+\Delta E_{\bar{n}}^-}{2mc^2+E_0+\Delta E_{\bar{n}}^-}\right)\right], \tag{15}$$

where we have introduced the relation

$$\Delta E_{\bar{n}}^- = -2mc^2 - E_{\bar{n}}^-. \tag{16}$$

When inserting the resolution of the identity it must be remembered that it includes the summation over both electronic and positronic solutions. Proper insertion in the first term on the right-hand-side (rhs) of Eq. (15) gives

$$\sum_{\bar{n}} \langle 0|H_1|\bar{n}\rangle\langle\bar{n}|H_1|0\rangle = \langle 0|H_1H_1|0\rangle - \sum_n \langle 0|H_1|n\rangle\langle n|H_1|0\rangle. \tag{17}$$

Substituting Eq. (17) into Eq. (15) we finally get

$$\sum_{\bar{n}} \frac{\langle 0|H_1|\bar{n}\rangle\langle\bar{n}|H_1|0\rangle}{E_0-E_{\bar{n}}^-} = \frac{1}{2mc^2}\left[\langle 0|H_1H_1|0\rangle - \sum_{n=0}^{\infty} |\langle 0|H_1|n\rangle|^2 - \sum_{\bar{n}} |\langle 0|H_1|\bar{n}\rangle|^2 \frac{(E_0+\Delta E_{\bar{n}}^-)}{2mc^2+E_0+\Delta E_{\bar{n}}^-}\right]. \tag{18}$$

The first term on the rhs of Eq. (18) gives the well-known diamagnetic term in the nonrelativistic limit. We would like to point out that Eq. (18) is exact and is fully relativistic. This means that even within the relativistic domain a diamagnetic expectation value term can be obtained (but it is only really useful if the two summations can be neglected). In all three terms of Eq. (18) the c-factors in H_1 cancel the c^2 in the $2mc^2$ denominator. The first term is thus of zeroth order in c. In the second term we have the matrix element of $\alpha\cdot\mathbf{A}$ between two electron solutions. This makes this term approximately of order $O(c^{-2})$, cf. Eq. (12). In the third term the matrix elements of $\alpha\cdot\mathbf{A}$ are taken between a positron and an electron solution which means that the upper (large) component of the electron solution is coupled to the lower (large) component of the positron solution, and they are, therefore, of zeroth order in c. However, the presence of the correction factor to the right involving $\Delta E_{\bar{n}}^-$ means that also the third term will be approximately of order $O(c^{-2})$, unless deep-lying positronic solutions with non-negligible $\Delta E_{\bar{n}}^-$ values compared to $2mc^2$ contribute significantly. Such solutions correspond in a way to positrons with large kinetic energy, i.e., they will oscillate rapidly and they are, therefore, unlikely to have any significant overlap with the reference electronic state through H_1 (as long as $\mathbf{A}$ is slowly oscillating). This indicates that also the third term will be small compared to the first. In Sec. II C 2 we outline a detailed procedure to check the validity of this assumption in the many-electron case.

When we insert Eq. (18) into Eq. (13) we end up with a modified (but exact) form of the second-order energy

$$E^{(2)} = \frac{\langle 0|H_1H_1|0\rangle - |\langle 0|H_1|0\rangle|^2}{2mc^2} + \sum_{n\neq 0} \frac{1-\frac{(E_0-E_n)}{2mc^2}}{E_0-E_n}\langle 0|H_1|n\rangle\langle n|H_1|0\rangle - \sum_{\bar{n}} \frac{(E_0+\Delta E_{\bar{n}}^-)}{2mc^2}\frac{\langle 0|H_1|\bar{n}\rangle\langle\bar{n}|H_1|0\rangle}{2mc^2+E_0+\Delta E_{\bar{n}}^-}, \tag{19}$$

that directly can be related to the nonrelativistic second-order energy by letting c approach infinity. The first term in the numerator of the first term becomes the diamagnetic term.

The second term in that numerator is for one-electron systems the square of the first-order energy correction divided by $2mc^2$, which gives a relativistic correction of order $O(c^{-2})$. For many-electron systems we shall later see that the correction is not simply the square of the first-order energy correction [Eq. (32)]. The second term in Eq. (19) goes to all the paramagnetic nonrelativistic terms (spin-independent as well as spin-dependent) in the nonrelativistic limit and the third term disappears because c goes to infinity and ΔE_n^- is equal to zero in that limit.

The relative contribution of the diamagnetic and paramagnetic terms is known to depend on the choice of gauge for the vector potential **A**. Only the sum of the two terms is gauge invariant in the limit of a complete basis set. This gauge dependence of the individual terms is easily explained by considering the resolution of identity in Eq. (17). Depending on the operator the contribution of the partial sums may vary and changing the gauge represents such a change of operator that does not affect the total second-order energy.

C. Many-electron case

1. Response theory

In the Mittleman picture, the no-pair Hamiltonian for the many-electron system is defined with respect to the total potential from the nuclei and the average repulsion from the other electrons (including exchange),[8] as discussed in Sec. II A. This is a *variational* condition and is, therefore, directly applicable to variational models as the single determinant, uncorrelated Dirac–Hartree–Fock (DHF) or a correlated model such as multiconfiguration Dirac–Hartree–Fock. We will in this section limit the discussion to the DHF approximation.

In this ''fuzzy'' picture the no-pair Hamiltonian is dynamically redefined during the wave function optimization process, such that it adapts to the average repulsion between the electrons as defined in the used wave function approximation. The implication of this is that the energy should be stationary with respect to mixing of electronic and positronic orbitals, in other words, that the energy should be stationary (and maximized) with respect to orbital rotations between the occupied electronic orbitals and the ''virtual'' positronic orbitals.[12,13] In a DHF calculation this is today routinely achieved through diagonalization of the total DHF matrix rather than the electron–electron block of the matrix. The latter would correspond to freezing the no-pair Hamiltonian. If, for example, electronic spinors were defined by initially diagonalizing the one-electron Dirac–Hamiltonian this would correspond to the Furry picture, with the problems discussed above in Sec. II A.

In order to continue the discussion we need a formalism for describing orbital rotations, and this is most conveniently done in the formalism of second quantization. We shall use the formalism introduced in the paper by Jensen *et al.* on four-component multiconfiguration self-consistent field models,[13] to which we refer for more details. This formalism, if expressed in terms of complex orbitals, has essentially the same structure in both relativistic and nonrelativistic theory. In the relativistic case the zeroth-order Hamiltonian is taken as the Dirac–Coulomb operator and the orbital basis consists of four-component spinors. At the (Dirac–)Hartree–Fock level of theory the wave function is defined by a set of parameters κ, which describe all nonredundant orbital rotations applied to a reference Slater-determinant

$$\Psi(\kappa)=\exp(-\hat{\kappa})\Psi(0)=\exp(-\hat{\kappa})|0\rangle,$$
$$\hat{\kappa}=\sum_{i,s}(\kappa_{si}\hat{a}_s^\dagger\hat{a}_i-\kappa_{si}^*\hat{a}_i^\dagger\hat{a}_s). \tag{20}$$

Indices s,t and i,j will be used for virtual and occupied orbitals, respectively. We now assume that our reference determinant is the fully optimized wave function with respect to the zeroth-order Hamiltonian. If we add a one-electron perturbation of field-strength ϵ

$$H_\epsilon=H_0+\epsilon H_1, \tag{21}$$

the wave function is no longer optimized. We may make a Taylor expansion with respect to the zeroth-order wave function in terms of the orbital parameters

$$\begin{aligned}E(\kappa)&=\langle 0|\exp(\hat{\kappa})H_\epsilon\exp(-\hat{\kappa})|0\rangle\\&=\langle 0|H_\epsilon|0\rangle+\langle 0|[\hat{\kappa},H_\epsilon]|0\rangle\\&\quad+\tfrac{1}{2}\langle 0|[\hat{\kappa},[\hat{\kappa},H_\epsilon]]|0\rangle+\cdots\\&=E(0)+\kappa^\dagger\mathbf{E}^{[1]}+\tfrac{1}{2}\kappa^\dagger\mathbf{E}^{[2]}\kappa+\cdots.\end{aligned} \tag{22}$$

The expansion defines the gradient $\mathbf{E}^{[1]}$ and Hessian $\mathbf{E}^{[2]}$ which corresponds to single and double derivatives, respectively, of the energy with respect to the wave function parameters κ, evaluated for the current orbitals ($\kappa=0$). Both quantities may be split into two parts corresponding to the two terms of the Hamiltonian [Eq. (21)], e.g.,

$$E_{si}^{[1]}=\left.\frac{\partial E}{\partial\kappa_{si}}\right|_{\kappa=0}=\langle 0|[\hat{a}_s^\dagger\hat{a}_i,H_0+\epsilon H_1]|0\rangle=E_{0;si}^{[1]}+\epsilon E_{1;si}^{[1]}. \tag{23}$$

Note that $\mathbf{E}_0^{[1]}=0$ since $\kappa=0$ corresponds to the wave function optimized with respect to the zeroth-order Hamiltonian.

Second-order properties are defined as second derivatives of the energy in terms of the perturbation parameter ϵ at zero field. As $\kappa=0$ at zero field ($\epsilon=0$), application of this definition to the Taylor expansion in Eq. (22) gives

$$\left.\frac{\partial^2 E}{\partial\epsilon^2}\right|_{\epsilon=0}=\left[2\left(\frac{\partial\kappa^\dagger}{\partial\epsilon}\right)\mathbf{E}_1^{[1]}+\left(\frac{\partial\kappa^\dagger}{\partial\epsilon}\right)\mathbf{E}_0^{[2]}\left(\frac{\partial\kappa}{\partial\epsilon}\right)\right]_{\epsilon=0}. \tag{24}$$

From time-independent perturbation theory[14] it follows that the first-order wave function (i.e., the correction linear in ϵ) is given by the parameters

$$\left.\frac{\partial\kappa}{\partial\epsilon}\right|_{\epsilon=0}=-(\mathbf{E}_0^{[2]})^{-1}\mathbf{E}_1^{[1]}. \tag{25}$$

Insertion of Eq. (25) into Eq. (24) gives the final expression

$$\left.\frac{\partial^2 E}{\partial\epsilon^2}\right|_{\epsilon=0}=-\mathbf{E}_1^{[1]\dagger}(\mathbf{E}_0^{[2]})^{-1}\mathbf{E}_1^{[1]}\equiv\mathrm{Re}\langle\langle H_1;H_1\rangle\rangle_{\omega=0}. \tag{26}$$

The identification of the second derivative of the energy with the polarization propagator at the random phase approximation (RPA) level for frequency independent properties $\mathrm{Re}\langle\langle H_1;H_1\rangle\rangle_{\omega=0}$ stems from the definition of the latter quantity (see e.g., Ref. 14). The expressions for magnetic and electric response properties in the relativistic polarization propagator approach were recently developed.[10,15]

2. The diamagnetic term in the many-electron case

Having developed the pertinent formulas we now turn our attention to the analysis of second-order magnetic properties within the framework of four-component relativistic theory. A major difference between nonrelativistic and relativistic response theory formulated in the language of second quantization is that in the latter case the orbital rotation parameters describe rotations between occupied electronic and virtual positronic orbitals ($e-p$ rotations) in *addition* to the rotations between occupied and virtual electronic spinors ($e-e$ rotations). The orbital rotation parameters thereby splits into two classes

$$\hat{\kappa}=\hat{\kappa}^e+\hat{\kappa}^p, \tag{27}$$

corresponding to $e-e$ and $e-p$ rotations, respectively. To distinguish the two classes of virtual orbitals we shall continue the convention of Sec. II B 2 and use overbar (e.g., $\overline{s}$) for positronic indices when needed.

The Hessian $\mathbf{E}_0^{[2]}$ of Eq. (26) corresponds to the principal propagator $\mathbf{P}$ of response theory in the frequency independent case and has the explicit form

$$\mathbf{P}^{-1}=\begin{bmatrix}\mathbf{A} & \mathbf{B}^*\\ \mathbf{B} & \mathbf{A}^*\end{bmatrix}^{-1},$$

$$\begin{cases} A_{si,tj}=\left.\dfrac{\partial^2 E}{\partial\kappa_{si}^*\partial\kappa_{tj}}\right|_{\kappa=0}=\delta_{st}\delta_{ij}(\epsilon_s-\epsilon_i)+(si|jt)-(st|ji)\\ B_{si,tj}=\left.\dfrac{\partial^2 E}{\partial\kappa_{si}^*\partial\kappa_{tj}^*}\right|_{\kappa=0}=(js|it)-(jt|is). \end{cases} \tag{28}$$

At this point it may be instructive to return to the one-electron case discussed in Sec. II B. The perturbational approach now corresponds to solving the response equation Eq. (25). Since all two-electron terms disappear we immediately recover the sum-over-states expression given in Eq. (13), and it becomes clear that leaving out κ_p gives only paramagnetic terms. Solving with both κ_e and κ_p gives the same result as Eq. (13), that is, it includes in addition the diamagnetic terms. This again shows that the inclusion of the positronic spinors corresponding to a redressing of the electrons caused by the *external magnetic field* is the origin of the diamagnetic term in the one-electron case.

We thus see that for the one-electron case this formulation based on second quantization and unitary rotations of the molecular orbitals gives the same answers as the traditional approach in previous sections. However, this formalism can be applied to the many-electron case. The sum over states formalism *cannot* be applied here, because states including positronic spinors are meaningless and wrong in the Dirac–Coulomb approach and should only be considered in a QED formulation. The inclusion of the positronic spinors in the spinor rotation operator as done here is correct and has a clear physical meaning: it describes the redressing of the electrons caused by the altered potential. For the following analysis it is convenient to slightly reorder the principal propagator [Eq. (28)] in order to separate $e-e$ and $e-p$ rotations. The principal propagator is then blocked in the following way:

$$\mathbf{P}^{-1}=\begin{bmatrix}\mathbf{A}_{ee} & \mathbf{B}_{ee}^* & \mathbf{A}_{ep} & \mathbf{B}_{ep}^*\\ \mathbf{B}_{ee} & \mathbf{A}_{ee}^* & \mathbf{B}_{ep} & \mathbf{A}_{ep}^*\\ \mathbf{A}_{pe} & \mathbf{B}_{pe}^* & \mathbf{A}_{pp} & \mathbf{B}_{pp}^*\\ \mathbf{B}_{pe} & \mathbf{A}_{pe}^* & \mathbf{B}_{pp} & \mathbf{A}_{pp}^*\end{bmatrix}^{-1}\equiv\begin{bmatrix}\mathbf{P}_{ee} & \mathbf{P}_{ep}\\ \mathbf{P}_{pe} & \mathbf{P}_{pp}\end{bmatrix}^{-1}. \tag{29}$$

The electronic subblock $\mathbf{P}_{ee}$ originating from κ_e is identical to the relativistic no-pair RPA propagator analyzed in Ref. 10. In Ref. 10 it was also shown that taking the nonrelativistic limit of these relativistic RPA equations in the no-pair approximation (that is, excluding κ_p) gives the nonrelativistic RPA equations for the paramagnetic terms. By analogy with the one-electron case, it follows that the diamagnetic term comes from the nonrelativistic limit of the κ_p block of the full relativistic RPA equations.

Let us analyze the order of magnitude of the different $\mathbf{A}$ and $\mathbf{B}$ matrix blocks of Eq. (29) using the explicit expressions in Eq. (28). Four types of two-electron integrals enter in these blocks. In the *ee*-block all spinors in the integrals are of the electronic type. Consequently the integrals are of order unity: $\mathrm{O}(c^0)$. In the *ep*- and *pe*-blocks one of the virtual spinors is of positronic type and the other virtual and the two occupied spinors are of electronic type. All integrals appearing in these blocks are thus of order $\mathrm{O}(c^{-1})$. In the *pp*-block the integrals representing a Coulombic interaction between positronic and occupied electronic spinors, i.e., $(\overline{st}|ji)$ in the *A* block, are of order unity, while all other integrals in the *A* block and all integrals in the *B* block are of order $\mathrm{O}(c^{-2})$.

From this analysis one may propose to neglect the *pe*- and *ep*-blocks of the principal propagator matrix in Eq. (29). In such a case the equation for the relativistic propagators will be divided in two branches, one for electronic–electronic virtual ($e-e$) excitations and another for electronic–positronic virtual ($e-p$) excitations, that is

$$\begin{aligned}\langle\langle H_1;H_1\rangle\rangle &\approx\langle\langle H_1;H_1\rangle\rangle_{ee}+\langle\langle H_1;H_1\rangle\rangle_{pp}\\ &=-\frac{1}{2}\left(\sum_{si,tj}E_{1;si}^{[1]*}(P_{ee}^{-1})_{si,tj}E_{1;tj}^{[1]}+\text{c.c.}\right)\\ &\quad-\frac{1}{2}\left(\sum_{\overline{si};\overline{tj}}E_{1;\overline{si}}^{[1]*}(P_{pp}^{-1})_{\overline{si},\overline{tj}}E_{1;\overline{tj}}^{[1]}+\text{c.c.}\right).\end{aligned} \tag{30}$$

The above expression is the response analogue in a spinor basis of Eq. (13) given in Sec. II B 2. The separation of the response function into an electronic and a positronic part forms the first step in a series of approximations leading to the replacement of the positronic response function by an expectation value corresponding to the diamagnetic term. The steps can be listed as follows:

0. The point of departure is the straightforward calculation of the linear response function $\langle\langle H_1;H_1\rangle\rangle$ at the RPA level of approach as given in Eq. (26) without any further approximations.

1. The first step in the hierarchy of approximations corresponds to neglecting the $\mathbf{P}_{ep}$ and $\mathbf{P}_{pe}$ blocks, i.e., the calculation of separate response functions for $e-e$ and $e-p$ rotations as outlined in Eq. (30).

2. In the positronic–positronic $\mathbf{P}_{pp}$ part of $\mathbf{P}$ we neglect $O(c^{-2})$ terms and we neglect the contribution of the $O(c^0)$ integrals $(\overline{st}|ji)$ compared with the energy difference $(\epsilon_{\overline{s}}-\epsilon_i)$, which is of the order of $-2mc^2$. We thus approximate $\mathbf{A}_{pp}$ by a diagonal matrix $\mathbf{A}^{pp}_{\overline{si},si}\approx\epsilon_{\overline{s}}-\epsilon_i$ and set the $\mathbf{B}_{pp}$ block equal to zero. The positronic response function can thereby be written as

$$\langle\langle H_1;H_1\rangle\rangle_{pp}\approx-\frac{1}{2}\left(\sum_{i,\overline{s}}\frac{\langle i|H_1|\overline{s}\rangle\langle\overline{s}|H_1|i\rangle}{\epsilon_{\overline{s}}-\epsilon_i}+\text{c.c.}\right)$$
$$=\sum_{i,\overline{s}}\frac{\langle i|H_1|\overline{s}\rangle\langle\overline{s}|H_1|i\rangle}{\epsilon_i-\epsilon_{\overline{s}}}, \tag{31}$$

which is analogous to the one-electron expression on the left-hand-side (lhs) of Eq. (15). We can, therefore, directly follow the one-electron analysis in the following steps. (When this approximation is applied to the $\mathbf{P}_{ee}$ block in nonrelativistic RPA this approach has been called the simple transition approximation,[16] and the approximation is very crude. Here the approximation is expected to be much better because $(\epsilon_i-\epsilon_{\overline{s}})$ is of order $2mc^2$.)

3. In the third step the denominator $(\epsilon_i-\epsilon_{\overline{s}})$ is replaced by $2mc^2$, which is a test of the Sternheim approximation.[1] The difference between steps 2 and 3 is then equivalent to the second term on the rhs of Eq. (15).

4. After insertion of the resolution of identity analogous to Eq. (17) and the perturbation operator [Eq. (10)] explicitly, one obtains

$$\langle\langle H_1;H_1\rangle\rangle_{pp}$$
$$\approx\frac{e^2}{2m}\sum_i\left(\langle i|A^2|i\rangle-\sum_j\langle i|\alpha\cdot\mathbf{A}|j\rangle\langle j|\alpha\cdot\mathbf{A}|i\rangle\right)$$
$$-\frac{e^2}{2m}\sum_{i,s}\langle i|\alpha\cdot\mathbf{A}|s\rangle\langle s|\alpha\cdot\mathbf{A}|i\rangle. \tag{32}$$

Differences between 3 and 4 will arise solely due to basis set incompleteness and present a measure for the adequacy of the basis set to calculate the diamagnetic term by explicit summation.

5. In the final step we retain only the expectation value corresponding to the diamagnetic term

$$\langle\langle H_1;H_1\rangle\rangle_{pp}\approx\frac{e^2}{2m}\sum_i\langle i|A^2|i\rangle=\frac{e^2}{2m}\langle 0|A^2|0\rangle. \tag{33}$$

This formulation resembles the nonrelativistic one and becomes exact in the nonrelativistic limit.

Similar approximation steps leading to a diamagnetic expectation value term can be done for multiconfiguration self-consistent field (MCSCF) wave functions.

III. CALCULATIONS ON THE *K*-TENSOR OF THE WATER ANALOGUES

Following the discussion presented above in Sec. II C 2 we will now investigate each approximation step for diamagnetic terms from ''approximation 0,'' the exact RPA expression in a finite basis, to ''approximation 5,'' the expectation value expression in Eq. (33), for a particular example. As an example we have chosen the diamagnetic spin–orbit term in calculations of reduced indirect spin–spin couplings for the water analogues, i.e., XH_2 model compounds (X=O, S, Se, and Te). The usual isotropic indirect nuclear spin coupling J^{MN} in Hz between nuclei M and N is related to the reduced coupling K^{MN} in SI units (i.e., $T^2J^{-1}=NA^{-2}m^{-3}$) by

$$hJ^{MN}=(\hbar^2\gamma_M\gamma_N)\quad K^{MN}, \tag{34}$$

where γ_M is the isotope dependent magnetogyric ratio for a specific isotope of nuclei M. We report the reduced couplings because they only depend on electronic effects, not on the specific isotope, and they can thus directly be compared between molecules in a series as the water analogues.

A. The reduced indirect nuclear spin–spin couplings, *K*

The indirect spin–spin coupling constants originate from the magnetic fields generated by the nuclei, and these perturbations correspond to a specific choice of the vector potential $\mathbf{A}$ (in atomic units)

$$\mathbf{A}=\sum_M\mathbf{A}_M=\sum_M\frac{\gamma_M}{c}\left(\mathbf{I}_M\times\frac{\mathbf{r}_M}{r_M^3}\right). \tag{35}$$

The magnetic operator may be written as (e is kept for clarity, although $e=1$ in atomic units)

$$H_1=ec\sum_M\alpha\cdot\mathbf{A}_M=-e\sum_M\gamma_M\mathbf{I}_M\cdot\kappa_M,$$
$$\text{where}\quad\kappa_M=\left(\alpha\times\frac{\mathbf{r}_M}{\mathbf{r}_M^3}\right). \tag{36}$$

Within the relativistic polarization propagator formalism $\mathbf{K}$ tensors can be written for coupling between nuclei M and N in the following form:[10]

$$K^{MN}_{ij}=e^2\,\text{Re}\langle\langle\kappa_{Mi};\kappa_{Nj}\rangle\rangle_{\omega=0}, \tag{37}$$

where i and j indicate Cartesian components (x,y,z). Equation (37) is in atomic units, the tensor $\mathbf{K}$ is usually reported in SI units, i.e., $T^2J^{-1}=NA^{-2}m^{-3}$.

B. Computational details

All Dirac–Hartree–Fock calculations and relativistic RPA calculations were performed with the DIRAC program package[17,18] with the Dirac–Coulomb–Hamiltonian as H_D. Calculations on H_2X (X=^{17}O, ^{33}S, ^{77}Se, ^{125}Te) were performed at the experimental geometries given in Table I. When experimental results are reported they correspond to the above mentioned isotopes.

Basis sets for H_2O and H_2S were constructed from the cc-pVDZ and cc-pVTZ sets in uncontracted form.[19] H(s) and O/S(s,p) exponents were taken from the cc-pVDZ set

TABLE I. Experimental geometries for H_2X model compounds.

Molecule	R(X–H)/Å	Angle (H–X–H)/degrees
H_2O[a]	0.972	104.50
H_2S[b]	1.328	92.20
H_2Se[c]	1.460	90.57
H_2Te[d]	1.659	90.26

[a]M. D. Harmony, V. W. Laurie, R. L. Kuczkowski, R. H. Schwendeman, D. A. Ramsey, F. J. Lovas, W. J. Lafferty, and A. G. Maki, J. Phys. Chem. Ref. Data **8**, 619 (1979).
[b]G. Herzberg, in *Molecular Spectra and Molecular Structure. III Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand, New York, 1966).
[c]T. Oka and Y. Morina, J. Mol. Spectr. **8**, 300 (1962).
[d]C. A. Mayhew and J. P. Connerade, J. Phys. B **19**, 3493 (1986).

and H(p) and O/S(d) functions were taken from the cc-pVTZ.[19] In addition five tight *s*-functions were added to each atomic species in an inward even-tempered series with $\beta=10$.

Basis sets for Se and Te were chosen as a relativistically optimized even tempered family basis using a modified[20] version of GRASP.[21] The defining parameters for relativistically optimized even tempered basis sets that were used are given in Table II. The even tempered formula for the kth Gaussian exponent is $\xi_k=\alpha\beta^{k-1}$ where k runs from 1 to the number of exponents N. A family basis is the result of making beta independent of the angular momentum and by choosing a common starting point for each series of exponents. Since these Se and Te basis sets were tested for the use in electric field gradient (EFG) calculations we also investigated the addition of tight *s*-functions that do not influence the EFG but may make a difference for the calculated spin–spin couplings. No significant changes were found upon adding three tight *s*-functions (exponents 10^7, 10^8, and $10^9 a_0^{-2}$) for Se and two tight *s*-functions (exponents 10^8 and $10^9 a_0^{-2}$) for Te. So the original basis was kept for both Se and Te. For Hydrogen in both the H_2Se and H_2Te model compounds we used Sadlej's basis set[22] in uncontracted form and augmented with a tight p (exponent $4.915\,78 a_0^{-2}$) and a d (exponent $0.710\,716 a_0^{-2}$) function.

In general the basis sets used here are not optimized for spin–spin coupling, and one cannot expect to get converged RPA results. However, they are sufficiently good for the purpose here, that is to study the diamagnetic term. To calculate good coupling constants close to experiment would also require inclusion of electron correlation and the correlation error is much greater than the basis set error (see e.g., the calculations on H_2O in Ref. 22).

C. Results and discussion

The results for ^1K(X,H) calculations of the different approximations defined in Sec. II C 2 are shown in Table III. It is seen that the experimental trend is reproduced: When the atom X is going down in the periodic table the ^1K(X,H) coupling is becoming more negative. No further comparison to experiment will be made, because the RPA model is poor for calculating spin–spin coupling constants. In nonrelativistic calculations this is caused by triplet instabilities or near triplet instabilities, which lead to a poor description of the triplet spectrum, and the problems carry over to the relativistic RPA. However, the diamagnetic spin orbit term (DSO) is a singlet property nonrelativistically and does not suffer the problems of the total value. The RPA model is, therefore, acceptable for the analysis of the DSO term.

The ''diamagnetic'' $e-p$ rotation contribution is very small in all ^{1}K(X,H) calculations. The contribution in H_2O is of the same order of magnitude as the DSO nonrelativistic contribution given previously by Geertsen and Oddershede (-0.0430).[23] The same authors obtained a total nonrelativistic RPA value for ^1K(O,H) of $+59.452$, which is close to ours. The differences can be attributed to our poorer basis set.

The results for the ^2K(H,H) calculations for the different approximations are shown in Table IV. It is seen that the $e-p$ rotation contribution is important for all four molecules, although the contribution is becoming smaller when X goes down the periodic table. The H_2O contribution (-0.5346) is close to that found by Geertsen and Oddershede (-0.5967).[23] When this contribution is calculated as an expectation value of A^2 (''Approx. 5'') the value is even closer (-0.5644), this effect will be discussed below. Previous nonrelativistic calculations of ^2K(H,H)[22] gave a value of -1.2868 which is close to ours. The main difference is in the $e-e$ contribution which corresponds to the Fermi contact, paramagnetic spin–orbit, and spin–dipolar terms and this reflects deficiencies in our basis set.

Let us now investigate the effect of the five approximation steps. Decoupling the *pp*-part of the propagator (''Approx. 1'') and using a diagonal approximation for this part (''Approx. 2'') give only very small changes as compared to the full RPA result (''Approx. 0''). The replacement of the diagonal by $-2mc^2$ gives a significant change for the X–H coupling for the heavier systems, but not for the H–H coupling (as seen in Table IV). We suggest that this reflects the nonrelativistic character of the wave functions near the light hydrogen nuclei, in the sense that the small components of all occupied spinors are very small close to the hydrogen nuclei. This indicates that the $\overline{n}$ spinors which contribute to

TABLE II. Defining parameters for the Selenium and Tellurium basis sets.

		s-set		*p*-set		*d*-set		*f*-set	
Atom	β	N	α	N	α	N	α	N	α
Selenium	2.378	23	0.019 428	16	0.046 201	12	0.046 201	3	0.109 872
Tellurium	2.240	27	0.018 705	21	0.018 705	15	0.041 904	4	0.093 878

TABLE III. ^1K(X,H) couplings for the different approximations described in Sec. II C 2.[a]

	H_2O		H_2S		H_2Se		H_2Te	
Approx.	$e-p$ rot.	Total	$e-p$ rot.	Total	$e-p$ rot.	Total	$e-p$ rot.	Total
0		57.8076		41.6398		25.1379		−24.1668
1	−0.0715	57.8062	−0.0321	41.6388	−0.0019	25.1382	0.0009	−24.1748
2	−0.0715	57.8062	−0.0321	41.6388	−0.0019	25.1382	0.0009	−24.1748
3	−0.0718	57.8059	−0.0327	41.6382	−0.0042	25.1358	−0.0028	−24.1784
4	0.0546	57.9323	0.0066	41.6775	−0.0049	25.1352	0.0022	−24.1734
5	0.0525	57.9302	0.0044	41.6754	−0.0054	25.1347	−0.0060	−24.1816
Exp.		+48.50[b]				+28.40[d]		+15.47[f]
		+49.52[c]				+28.07[e]		

[a]K is given in $10^{19}\,T^2\,J^{-1}$. Magnetogyric ratios are given in 10^7 rad $s^{-1}\,T^{-1}$. They are for ^{1}H, 26.7522; ^{17}O, −3.6281; ^{33}S, 2.0557; ^{77}Se, 5.1251; ^{125}Te, −8.5108. The results for the pure $e-e$ rotations in approximations 1–5 are: H_2O, 57.8777; H_2S, 41.6709; H_2Se, 25.1401; H_2Te, −24.1757.
[b]C. Canet, C. Goulon-Ginet, and J. P. Marchal, J. Magn. Reson. **22**, 539 (1976); **25**, 397 (1977).
[c]N. M. Sergeyev, N. D. Sergeyeva, Yua. A. Strelenko, and W. T. Raynes, Chem. Phys. Lett. **277**, 142 (1997).
[d]Taken from C. J. Jameson, in *Multinuclear NMR*, J. Mason De. (Plenum, New York, 1989).
[e]H. Dreeskamp and G. Pfisterer, Mol. Phys. **14**, 295 (1968).
[f]C. Glidewell, D. W. A. Rankin, and G. M. Sheldrick, Trans. Farad. Soc. **65**, 1409 (1969).

the $e-p$ rotations for the hydrogens will have very small large components and thus energy differences close to the free-particle limit of $2mc^2$. The same argument can be used for the light Oxygen and fairly light Sulphur nuclei.

From ''Approx. 3'' to ''Approx. 4'' the finite basis set summation is substituted with the resolution of identity, which gives a significant effect for all the couplings calculated. This indicates that the basis sets used are not complete. Part of this is due to the use of a small component basis set that is designed to satisfy the kinetic balance relation as dictated by the $\alpha\cdot\mathbf{p}$ operator (restricted kinetic balance, RKB), while the present response calculations gauge the completeness with respect to the $\alpha\cdot\mathbf{A}$ operator [compare Eqs. (6) and (12)]. A convenient, but far from optimal, way to extend the positronic space is to use a so-called unrestricted kinetically balanced basis set (UKB). In this method one represents both the large and small component functions with Cartesian Gaussian type functions, eliminating the $3s$ and higher contaminant functions only in the large component. This gives a small component basis set that is larger in size than the conventional restricted type basis set (in which each large component function is balanced by precisely one small component function), without significantly increasing the computational effort. We have done a series of calculations on water in which the unrestricted formalism was used and find that the transition from ''Approx. 3'' to ''Approx. 4'' is indeed more smooth than in the restricted formalism (see Table V). This can be understood from the form of the $\alpha\cdot\mathbf{A}$ operator [see Eq. (36)]. This operator is multiplicative, which means it couples a large component l-type basis function with a small component $(l+1)$-type basis function, while the $\alpha\cdot\mathbf{p}$ operator couples with a fixed combination of a small component $(l-1)$-type and $(l+1)$-type basis function, this fixed combination is the RKB. In UKB small component $(l-1)$-type and $(l+1)$-type basis functions are kept as separate functions, and it is thus clear why the UKB performs better in Table V.

Practical application of this scheme is, however, hampered by numerical instabilities due to the increasing linear dependency in such a basis. This made it impractical to use the unrestricted scheme in the calculations on the heavier dihydrides in our current implementation. A way to proceed is in principle to generalize the kinetic balance relation and introduce an additional set of ''magnetically balanced'' basis functions. Given the form of the $\alpha\cdot\mathbf{A}$ operator this will, however, lead to much more complicated basis functions.

TABLE IV. ^{2}K(H,H) calculated couplings for the different approximations described in the text.[a]

	H_2O		H_2S		H_2Se		H_2Te	
Approx.	$e-p$ rot.	Total	$e-p$ rot.	Total	$e-p$ rot.	Total	$e-p$ rot.	Total
0		−1.9410		−1.7168		−1.9877		−1.9518
1	−0.5346	−1.9410	−0.1353	−1.7168	−0.1194	−1.9877	−0.0893	−1.9518
2	−0.5346	−1.9410	−0.1353	−1.7168	−0.1194	−1.9877	−0.0893	−1.9518
3	−0.5348	−1.9412	−0.1353	−1.7168	−0.1194	−1.9877	−0.0893	−1.9518
4	−0.5640	−1.9703	−0.1531	−1.7346	−0.1340	−2.0024	−0.0994	−1.9619
5	−0.5641	−1.9705	−0.1531	−1.7346	−0.1340	−2.0024	−0.0994	−1.9619
Exp.		±0.60[b]						

[a]K is given in $10^{19}\,T^2\,J^{-1}$. The results for the pure $e-e$ rotations in approximations 1–5 are: H_2O, −1.4064; H_2S, −1.5815; H_2Se, −1.8684; H_2Te, −1.8625.
[b]J. R. Holmes, D. Kivelson, and W. C. Drinkard, J. Chem. Phys. **37**, 150 (1962).

TABLE V. Contributions to total ^1K(O,H) and ^2K(H,H) using RKB and UKB conditions for the H_2O molecule.[a]

	^1K(O,H)				^2K(H,H)			
	$e-p$ rot.		Total		$e-p$ rot.		Total	
Approx.	RKB	UKB	RKB	UKB	RKB	UKB	RKB	UKB
0			57.8076	58.1209			−1.9410	−1.9685
1	−0.0715	0.0585	57.8062	58.1196	−0.5346	−0.5590	−1.9410	−1.9684
2	−0.0715	0.0585	57.8062	58.1196	−0.5346	−0.5590	−1.9410	−1.9685
3	−0.0718	0.0585	57.8059	58.1196	−0.5348	−0.5592	−1.9412	−1.9687
4	0.0546	0.0581	57.9323	58.1192	−0.5640	−0.5640	−1.9703	−1.9734
5	0.0525	0.0526	57.9302	58.1137	−0.5641	−0.5641	−1.9705	−1.9735

[a]K is given in $10^{19}\,T^2\,J^{-1}$. Results of $e-e$ rotations are: (i) for ^1K(O,H), RKB=57.8777 and UKB =58.0611; (ii) for ^2K(H,H), RKB=−1.4064 and UKB=−1.4094.

IV. CONCLUSIONS

In this paper we have given a new insight on different contributions to magnetic properties. Starting from a fully relativistic formulation the origin of diamagnetic terms for magnetic properties is clear: When a magnetic field is applied to a molecular system the electronic spinors are modified in such a way that contributions from positronic spinors should be considered in calculating the response of the system to the external field.

Both paramagnetic and diamagnetic terms in nonrelativistic formalisms are obtained from a single operator [Eq. (4)] in the relativistic domain. This means that the separation in two parts arises from manipulation. As summarized in Sec. II B 1 the nonrelativistic diamagnetic contribution appears naturally for one-electron systems when the magnetic interaction is included from the outset in the Dirac equation. On the other side, considering electronic and positronic one-electron states obtained for the system in absence of a magnetic field, the nonrelativistic diamagnetic contribution appears in perturbation theory if and only if the positronic states are taken into account (Sec. II B 2), as shown before.[1,2] The fully relativistic second-order energy correction for one-electron systems as written in Eq. (19) shows that it can be divided into three terms; the first two can be identified as diamagnetic like and paramagneticlike and the third term disappears if c goes to infinity. The first two terms are completely in terms of electronic spinors while the last term includes positronic spinors explicitly.

In the many-electron case propagator methods are frequently used in the nonrelativistic domain to calculate magnetic properties. In this paper we used relativistic polarization propagators at the RPA level to show that the diamagnetic contribution arises exclusively from the *pp* block of the principal propagator [see Eq. (30)] when the *ep* part of it is neglected. From our results the difference between step 0 and step 1 pointed out in Sec. II C 2 is vanishingly small for XH_2 model compounds. This means that the *ep* part of **P** in Eq. (29) is negligible compared with the other parts of **P**.

Calculated NMR-K values with a fully relativistic code are presented. The well-known experimental trend for ^1K(X,H) couplings in XH_2-type molecules is qualitatively reproduced. Our numerical results show that calculating the diamagnetic contribution to the reduced nuclear spin coupling as a relativistic four-component expectation value of A^2 is quite a good approximation to its RPA value for the model compounds. It is also shown that Sternheim's one-electron approximation can be applied with confidence in these many-electron cases. As another interesting result we suggest that the difference between steps 3 and 4 can be used as a test of basis set completeness for magnetic properties. UKB basis sets may be used to obtain improved ''magnetic balance,'' but care must be used to avoid numerical problems.

ACKNOWLEDGMENTS

G.A.A. was partially supported by the Danish Natural Science Research Council (Grant No. 9600856), T.S. was supported by Carlsbergfondet (Grant No. 950340/20), and L.V. was supported by the European Union (Contract ERBFMBICT960738). The computations were supported by the Danish Natural Science Research Council (Grant No. 9313314).

[1] M. M. Sternheim, Phys. Rev. **128**, 676 (1962).
[2] P. Pyykkö, Chem. Phys. **74**, 1 (1983).
[3] J. Sucher, Phys. Rev. A **22**, 348 (1980).
[4] G. E. Brown and D. G. Ravenhall, Proc. R. Soc. London, Ser. A **208**, 552 (1951).
[5] P. A. M. Dirac, Proc. R. Soc. London, Ser. A **117**, 610 (1928); **118**, 351 (1928).
[6] J. Sucher, in *Relativistic, Quantum Electrodynamic and Weak Interaction Effects in Atoms* (AIP Conference Proceeding 189, New York, 1989).
[7] W. H. Furry, Phys. Rev. **81**, 115 (1951).
[8] M. H. Mittleman, Phys. Rev. A **24**, 1167 (1981).
[9] J.-L. Heully, I. Lindgren, E. Lindroth, and A.-M. Mårtensson-Pendrill, Phys. Rev. A **33**, 4426 (1986).
[10] G. A. Aucar and J. Oddershede, Int. J. Quantum Chem. **47**, 425 (1993).
[11] W. Kutzelnigg, Theor. Chim. Acta **73**, 173 (1988).
[12] J. D. Talman, Phys. Rev. Lett. **57**, 1091 (1986).
[13] H. J. Aa. Jensen, K. G. Dyall, T. Saue, and K. Fægri, Jr., J. Chem. Phys. **104**, 4083 (1996).
[14] J. Oddershede, P. Jørgensen, and D. L. Yeager, Comput. Phys. Rep. **2**, 33 (1984); J. Olsen and P. Jørgensen, J. Chem. Phys. **82**, 3235 (1985); P. Jørgensen, H. J. Aa. Jensen, and J. Olsen, *ibid.* **89**, 3654 (1988).
[15] L. Visscher, T. Saue, and J. Oddershede, Chem. Phys. Lett. **274**, 181 (1997).
[16] T. H. Dunning and V. McKoy, J. Chem. Phys. **47**, 1735 (1967).
[17] T. Saue, K. Fægri, Jr., T. Helgaker, and O. Gropen, Mol. Phys. **91**, 937 (1997).

[18] T. Saue and H. J. Aa. Jensen (to be published).
[19] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989); D. E. Woon and T. H. Dunning, Jr., *ibid.* **98**, 1358 (1993).
[20] K. G. Dyall and K. Fægri, Jr., Theor. Chim. Acta **94**, 39 (1996).
[21] K. G. Dyall, I. P. Grant, C. T. Johnson, E. P. Plummer, and F. Parpia, Comput. Phys. Commun. **55**, 425 (1989).
[22] A. Sadlej, Collect. Czech. Chem. Commun. **53**, 1995 (1988).
[23] J. Geertsen and J. Oddershede, Chem. Phys. **90**, 301 (1984).